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UNIVERSITI SAINS MALAYSIA

First Semester Examination  
2009/2010 Academic Session

November 2009

**KOE223 – Organic Chemistry Mechanisms**  
***[Mekanisme Dalam Tindak Balas Organik]***

Duration: 2 hours  
*[Masa : 2 jam]*

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Please check that this examination paper consists of TEN pages of printed material before you begin the examination.

**Instructions:**

Answer any **FOUR** (4) questions.

Answer each question on a new page.

You may answer either in Bahasa Malaysia or in English.

If a candidate answers more than four questions, only the answers to the first four questions in the answer sheet will be graded.

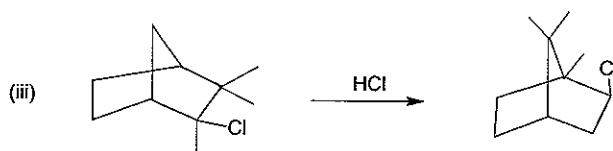
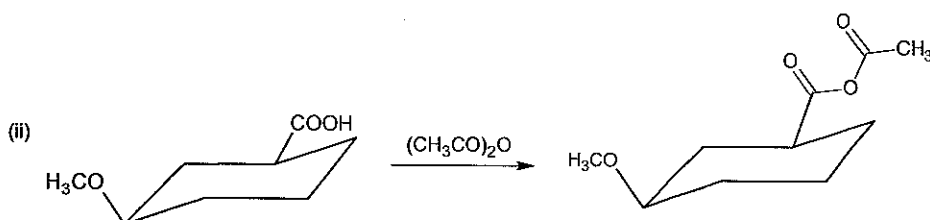
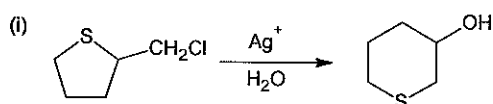
In the event of any discrepancies, the English version shall be used.

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1. (a) What is isotopic labeling? Why is isotopic labeling important in the study of reaction mechanisms? (7 marks)
- (b) Explain how isotopic labeling is used in elucidating the acid-catalysed esterification reaction. (10 marks)
- (c) On heating at 260 °C for five hours, (+)-PhMeEtCNC rearranges to PhMeEtCCN which is optically inactive. Suggest a mechanism for this reaction and give account for the loss of optical activity. (8 marks)

2. (a) Use the reaction of one equivalent of HCl with (i) of the compound below to explain the meaning of kinetic and thermodynamic control. Give the possible product obtained from the reaction
- (i) 2,3-dimethyl-1,3-pentadiene  
 (ii) 2,4-dimethyl-1,3-pentadiene  
 (iii) 1,3-butadiene
- (b) For each reaction indicate the kinetic and thermodynamic products. Give an intermediate for each of reactions above. (15 marks)

- (c) Propose a mechanism for each of the following reactions:



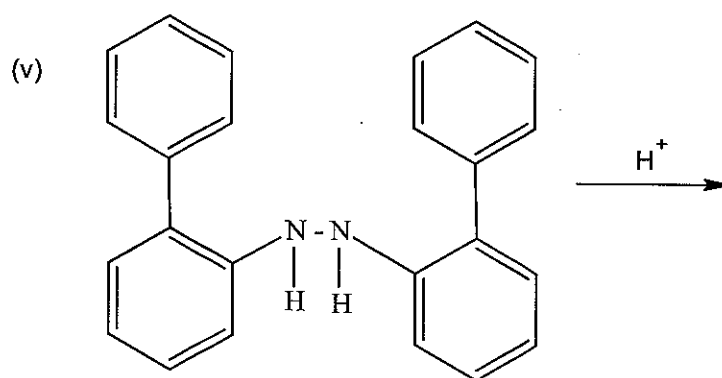
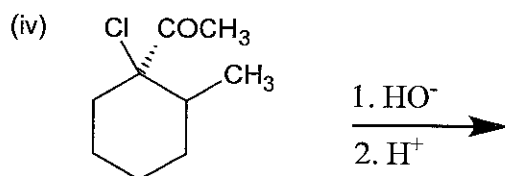
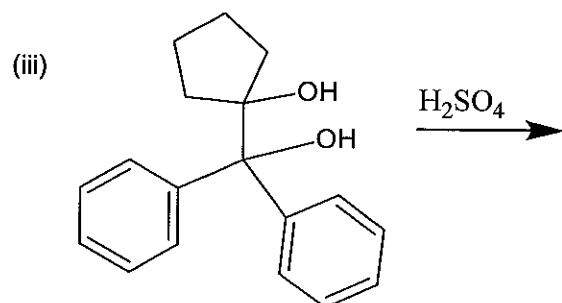
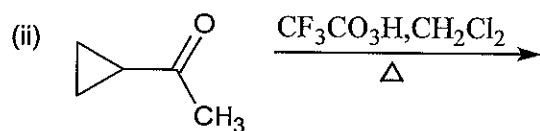
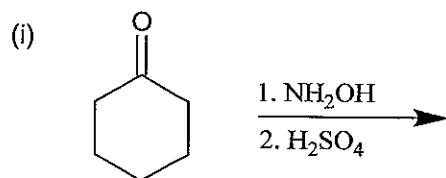
(10 marks)

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3. (a) Give the major types of intermediates. (5 marks)
- (b) State, by providing an example:
- (i) How each type of intermediate may be trapped?
- (iii) How each type of intermediate can be detected? (14 marks)
- (c) Give the structure and type for the intermediate species designated by:
- i)  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3 + \text{H}^+ \xrightarrow{\text{heat}} ? + \text{H}_2\text{O}$
- ii)  $\text{CH}_3\text{CH}=\text{CHCH}_3 + \text{HI} \longrightarrow ? + \text{I}^-$
- iii)  $\text{CH}_3\text{CH}_2\text{N}=\text{NCH}_2\text{CH}_3 \xrightarrow{\text{heat}} ? + \text{N}\equiv\text{N}$
- iv)  $\text{CH}_3\text{CHI}_2 + \text{Zn} \longrightarrow ? + \text{ZnI}_2$
- v)  $\text{CH}_3\text{CH}_2\text{Cl} + \text{AlCl}_3 \longrightarrow ? + [\text{AlCl}_4]^-$
- vi)  $\text{CH}_3-\text{C}\equiv\text{CH} + \text{Na}^+ :\text{NH}_2^- \longrightarrow ? \text{Na}^+ + \text{NH}_3$  (6 marks)
4. (a) Write down the Hammett equation in its ordinary form. Define the parameters  $\sigma$  and  $\rho$ , and explain how Hammett obtained his original scale of  $\sigma$  values. (8 marks)
- (b) In its ordinary form the equation had limited applicability, and the original compilation of  $\sigma$  constants was supplemented by inclusion of  $\sigma^0$ ,  $\sigma^+$  and  $\sigma^-$  values. What are these values and why did people feel they were necessary/advantageous? (8 marks)
- (c) Further elaboration has resulted in a number of attempts to resolve substituent constants into fixed and variable components. One of these was the complete resolution of Ehrenson, Brownlee, and Taft.
- (i) Give the equation proposed by the group.
- (ii) What is (are) its advantage(s) over the original Hammett equation?
- (iii) Equation (c) (i) does not represent a truly satisfactory solution to the problem. What is this problem and why does it arise? (9 marks)

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5. (a) Predict the product for each of the following reactions:



(15 marks)

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- (b) (i) Draw the energy profile for the reaction of iodomethane with ethoxide ion in ethanol.



- (ii) Label  $\Delta H$ ,  $E_a$  and a transition state.
- (iii) Draw the transition state for this reaction.

(10 marks)

## TERJEMAHAN

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### Arahan:

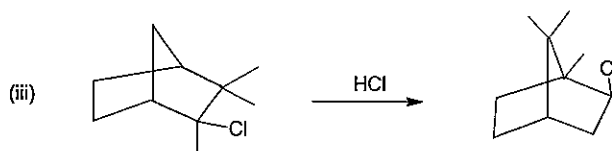
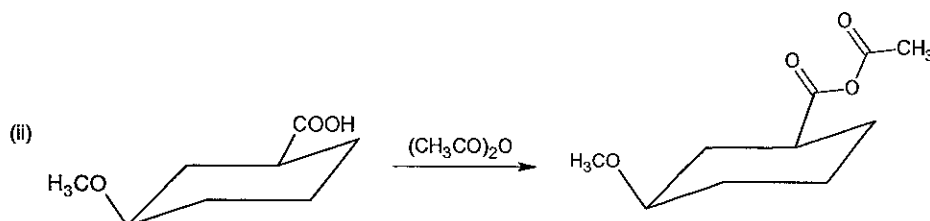
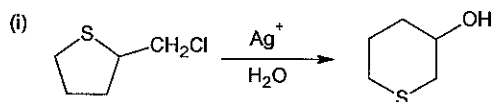
Jawab EMPAT (4) soalan.

Anda dibenarkan menjawab soalan ini sama ada dalam Bahasa Malaysia atau Bahasa Inggeris.

Jika calon menjawab lebih daripada empat soalan, hanya empat soalan pertama mengikut susunan dalam skrip jawapan akan diberi markah.

Sekiranya terdapat sebarang percanggahan pada soalan peperiksaan, versi Bahasa Inggeris hendaklah diguna pakai.

1. (a) Apakah perlabelan isotopik? Mengapa perlabelan isotopik penting dalam kajian tentang mekanisme tindak balas? (7 markah)
  - (b) Terangkan bagaimana pelabelan isotop digunakan dalam tindakbalas pengesteran pemangkinan asid? (10 markah)
  - (c) Apabila dipanaskan pada suhu 260 °C untuk jam (+)-PhMeEtCNC menyusun semula menjadi PhMeEtCCN yang tidak aktif optik cadangkan mekanisme untuk tindak balas ini dan pertimbangan yang sesuai bagi kehilangan aktiviti optik tersebut. (8 markah)
2. (a) Gunakan tindak balas satu equivalen HCl dengan (i) sebatian dibawah untuk menerangkan kawalan kinetik dan termodinamik? Berikan hasil yang mungkin diperolehi daripada tindak balas tersebut.
    - (i) 2,3-dimetil-1,3-pentadiena
    - (ii) 2,4-dimetil-1,3-pentadiena
    - (iii) 1,3-butadiena
  - (b) Bagi setiap tindakbalas tentukan hasil Kinetik dan Termodinamik. Berikan bahan perantara kedua tindak balas di atas. (15 markah)
  - (c) Cadangkan suatu mekanisme bagi setiap tindak balas berikut:



(10 markah)

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3. (a) Berikan jenis bahan perantara utama

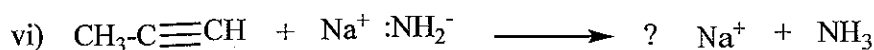
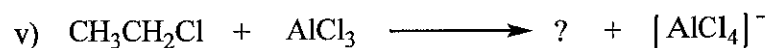
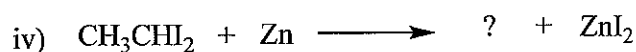
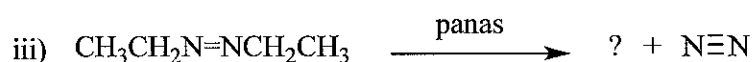
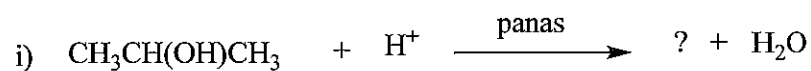
(5 markah)

- (b) Jelaskan dengan member contoh,

- (i) Bagaimana setiap jenis bahan perantara diperangkap?  
 (ii) Bagaimana setiap jenis bahan perantara dikesan?

(14 markah)

- (c) Berikan struktur dan jenis bahan perantara bagi:



(6 markah)

4. (a) Tuliskan persamaan Hammett. Nyatakan definisi parameter  $\sigma$  dan  $\rho$ . Jelaskan tanda dan magnitud kedua-dua parameter tersebut.

(8 markah)

- (b) Aplikasi persamaan Hammett yang asal adalah terhad dan penyusunan asal pemalar  $\sigma$  telah ditambah oleh kemasukan nilai  $\sigma^0$ ,  $\sigma^+$  dan  $\sigma^-$ . Apakah nilai-nilai tersebut dan mengapa ia diperlukan/lebih sesuai digunakan.

(8 markah)

- (c) Huraian yang selanjutnya telah menghasilkan beberapa percubaan untuk menyelesaikan pemalar tetap penukarganti kepada komponen tetap dan komponen berubah. Satu daripadanya ialah resolusi lengkap oleh kumpulan Ekrenon, Brownlee, dan Taft.

- (i) Tuliskan persamaan yang dicadangkan oleh kumpulan tersebut.  
 (ii) Apakah kelebihan persamaan yang dinyatakan dalam bahagian (c) (i) dibandingkan dengan persamaan Hammett?

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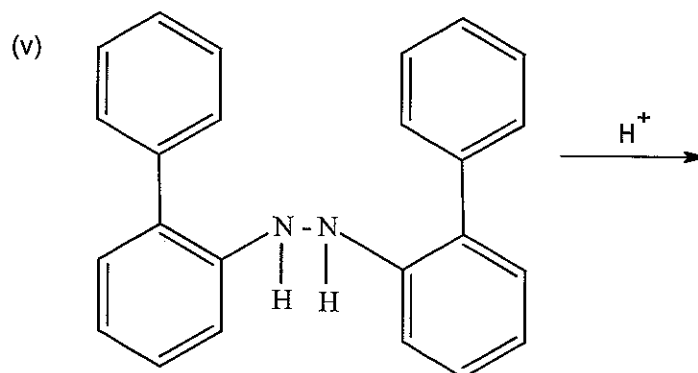
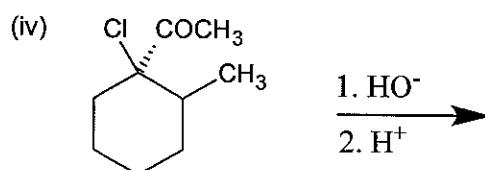
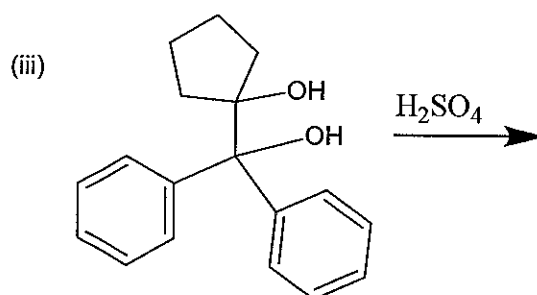
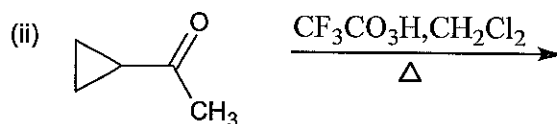
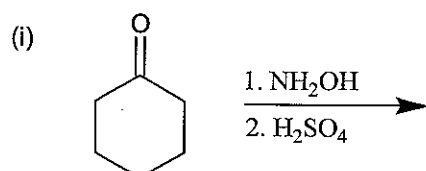


- (iii) Persamaan (c) (i) bukan satu penyelesaian yang memuaskan terhadap masalah yang dihadapi. Apakah masalah tersebut dan mengapa terjadinya masalah ini?

(9 markah)

5.

- (a) Ramalkan hasil untuk setiap tindak balas berikut:



(15 markah)

-10-

- (b) (i) Lukiskan lakaran tenaga untuk tindak balas iometana dengan ion etoksida dalam etanol
- $$\text{EtO}^- + \text{MeI} \longrightarrow \text{EtO-Me} + \text{I}^-$$
- (ii) Labelkan  $\Delta H$ ,  $E_a$  dan keadaan peralihan.
- (iii) Lukiskan keadaan peralihan dan bahan perantaraan bagi tindak balas tersebut.

(10 markah)

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